Improving the biorefinery output by coupling ethanol fermentation, anaerobic digestion and pyrolysis

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1. Background and Methodology

An effective transition from a fossil-based economy to a bio-based economy requires sustainable biomass resources and meticulously designed biorefinery schemes. This work presents a compilation of multiple pyrolysis experiments, starting from two different digestates, hence, different biorefinery schemes. The first digestate was obtained from poplar coppice upon sequential bisulfate pretreatment, ethanol fermentation and anaerobic digestion (Fig. 1). This digestate was referred to as "lignin-rich digested stillage" (LRDS). The second digestate resulted from anaerobic digestion of cocoa pod husks, referred to as "cocoa digestate" (Fig. 1). While LRDS can be considered as an emerging residue from lignocellulosic ethanol production, cocoa pod husks are voluminous residues from cocoa production.

The LRDS was subjected to slow pyrolysis and fast pyrolysis. Slow pyrolysis of the digested stillage was performed in a fixed bed reactor at a pyrolysis temperature of 370 °C and 450 °C. Fast pyrolysis of the digested stillage was performed in a stirred bed reactor at 480 °C. Cocoa pod husks were subjected to slow pyrolysis at a pyrolysis temperature of 350 °C and 500 °C, in a fixed bed reactor.

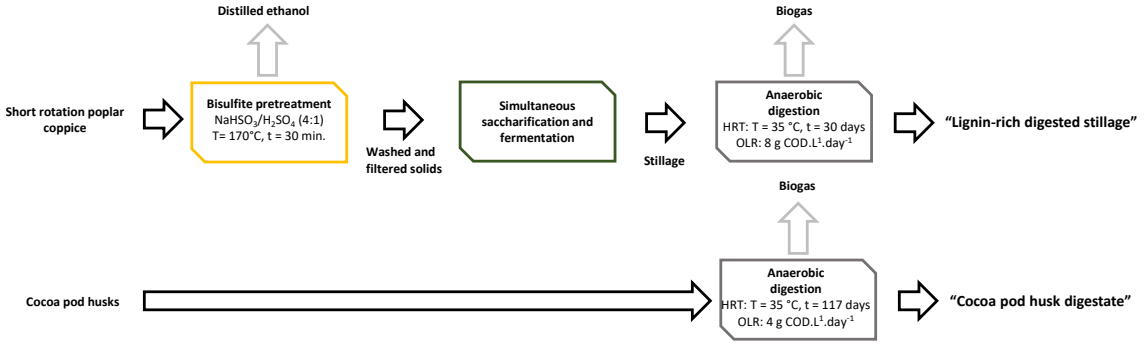

Figure 1: Specifics for the biological processing of poplar coppice (top) and cocoa pod husks (bottom).

The LRDS and cocoa digestate, as well as obtained biochars, were characterized through elemental analysis. Pyrolysis liquids (organic phase) from raw and digested cocoa pods were analyzed through GC-MS, while pyrolysis liquids (organic phase) from lignin-rich digested stillage were analyzed though GCxGC-FID analysis.

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2. Results and Discussions

Table 1 and Fig. 2 present the results from slow pyrolysis of raw cocoa pods, cocoa digestate, raw poplar and LRDS. The yields in biochar from (digested) cocoa pods were on the higher end of typical biochar yields from lignocellulosic biomass, while the yields in biochar for poplar-derived lignin-rich digested stillage were higher (Weber and Quicker, 2018). This was due to the the high Klasson lignin content (ca. 63%) of the digested stillage.

The elevated biochar yield from LRDS was remarkably higher than that of raw poplar (Table 1). For cocoa pods and digested cocoa pods, similar biochar yields were obtained. The reason for this difference in biochar yield between the lignin-rich digested stillage and digested cocoa was that the digested stillage was more lignin-rich, compared to the cocoa digestate. This on its turn was explained by e.g. the extra bisufite pretreatment, enhancing carbohydrate accessibility during ethanol fermentation and digestion.

Table 1: Yield in biochar from slow pyrolysis for their associated pyrolsis temperature. LRDS: lignin-rich digested stillage. Poplar data from Wu et al. (2018), LRDS data from Ghysels et al. (2019).

Yield (wt.%)										
Cocoa			Cocoa digestate			Poplar		LRDS		
T °C	av	stdev	T °C	av	stdev	T °C	av range	T °C	av	stdev
350	49.20	0.57	350	48.00	0.00			370	52.17	1.93
						410	32 to 35	410	47.75	1.76
500	39.00	0.28	500	38.50	0.14	450	28 to 32	450	45.14	1.40

The chemical changes from the raw feedstock, over the biologically pretreated ones, to the corresponding biochars are apparent from Fig. 2 (left). The O/C ratio clearly decreased from the raw poplar and raw cocoa pods to the biologically pretreated equivalents, although more pronounced for the LRDS. Such extensive decrease in O/C ratio from poplar to the LRDS also endorses its high lignin content and the associated elevated biochar yields. Moreover, it is clear that a prior digestion improved (i.e. lowered) the O/C ratio, compared to the raw feedstocks. Hence the carbonization and expected biochar stability are improved. The ranking of O/C ratio's was e.g. cooa pods (0.66) > digested cocoa pods (0.62) > cocoa pods biochar 350 °C (0.32) > digested cocoa pods biochar 350 °C (0.27) > cocoa pods biochar 500 °C (0.17) > digested cocoa pods biochar 500 °C (0.10).

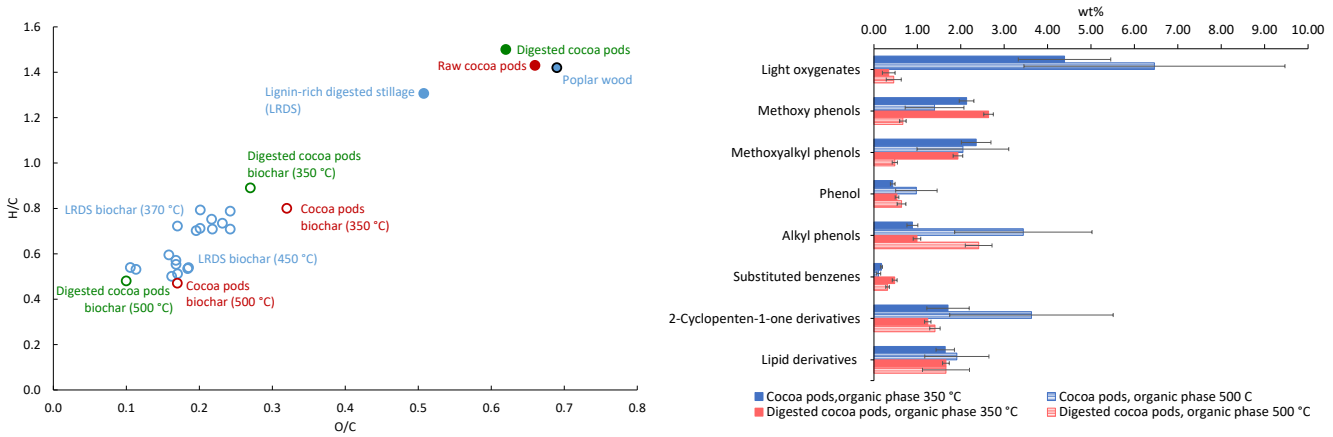

Figure 2: Left: Van Krevelen diagram with data on lignin-rich digested stillage (Ghysels et al. (2019)), poplar (Chen et al. (2016)) and (digested) cocoa. Right: composition of the organic phase of pyrolysis liquids from slow pyrolysis of cocoa pods and digested cocoa pods at 350 °C and 500 °C.

The chemical composition of the organic phase (Fig. 2, right) also demonstrates the changed biocomposition from the raw cocoa pods to the digested cocoa pods. The carbohydrate-derived "2-cyclopenten-

1-one derivatives" and "light oxygenates" in the organic phase from pyrolysis of digested cocoa pods at 500 °C merely increased, compared to the content of "2-cyclopenten-1-one derivatives" and "light oxygenates" in liquids from pyrolysis at 350 °C. This suggests that a significant fraction of the cellulose was already digested. Cellulose volatilization is incomplete at 350 °C (Venderbosch and Prins, 2010). Therefore, an increase of "2-cyclopenten-1-one derivatives" and "light oxygenates" in pyrolysis liquids of carbohydrate-containing feedstocks from pyrolysis at 500 °C would be expected. Not observing these increases (Fig. 2, right) indicates the smaller contribution of cellulose in the cocoa digestate (compared to raw cocoa pod) that would decompose beyond 350 °C. From a valorization point-of-view, its noteworthy that pyrolysis of digestate increased the content of valuable phenolics (Mahmood et al., 2016) within the liquids, compared to the raw feedstock.

For the obtained pyrolysis liquids, the ratio of carbohydrate-derived compounds over lignin-derived compounds was calculated to quickly evaluate the effect of the biological pretreatment(s) on the pyrolysis liquids' quality. For the raw cocoa pods, this ratio was 1.27, while that for digested cocoa was 0.41 (both from pyrolysis at 500 °C). The ratio of carbohydrate-derived compounds over lignin-derived compounds in fast pyrolysis liquids from LRDS at 480 °C was 0.40. Pyrolysis of the LRDS and cocoa digestate thus resulted in approx. the same ratio. The drop from 1.27 (for liquids from raw cocoa pods) to 0.41 (for liquids from digested cocoa) once more confirms that carbohydrates have partly been valorized to biogas, leaving a phenolics-rich oil for chemical valorization (Mahmood et al., 2016).

So, all in all, co-generation of ethanol and/or biogas is realized, together with high-quality (i.e. low O/C) biochar and phenolics-rich pyrolysis liquids. Hence, the integrated biorefinery improved its output portfolio.

3. Conclusions

Coupling the biological processes (i.e. ethanol fermentation and/or anaerobic digestion) with pyrolysis improves the biorefinery output, because: (i) carbohydrates are valorized to ethanol and/or biogas, rather than ending up as "light oxygenates" in the aqueous pyrolysis liquids, (ii) pyrolysis liquids are enriched in the phenolics, which are considered valuable precursors for further biorefining (Huang et al., 2018) and (iii) biohars are obtained with a higher degree of carbonization and stability (in terms of O/C ratio) after prior fermentation and/or digestion, and at a higher yield in case of sequential ethanol fermentation and anaerobic digestion.

References

Chen, D., Li, Y., Cen, K., Luo, M., Li, H., Lu, B., 2016. Pyrolysis polygeneration of poplar wood: Effect of heating rate and pyrolysis temperature. Bioresource Technology 218, 780 – 788.

Ghysels, S., Ronsse, F., Dickinson, D., Prins, W., 2019. Production and characterization of slow pyrolysis biochar from lignin-rich digested stillage from lignocellulosic ethanol production. Biomass and Bioenergy 122, 349 – 360.

Huang, Y., Duan, Y., Qiu, S., Wang, M., Ju, C., Cao, H., Fang, Y., Tan, T., 2018. Lignin-first biorefinery: a reusable catalyst for lignin depolymerization and application of lignin oil to jet fuel aromatics and polyurethane feedstock. Sustainable Energy Fuels 2, 637–647.

Mahmood, N., Yuan, Z., Schmidt, J., Xu, C.C., 2016. Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review. Renewable and Sustainable Energy Reviews 60, 317 – 329.

Venderbosch, R., Prins, W., 2010. Fast pyrolysis technology development. Biofuels, Bioproducts and Biorefining 4, 178–208.

Weber, K., Quicker, P., 2018. Properties of biochar. Fuel 217, 240 – 261.

Wu, X.F., Zhou, Q., Li, M.F., Li, S.X., Bian, J., Peng, F., 2018. Conversion of poplar into bio-oil via subcritical hydrothermal liquefaction: Structure and antioxidant capacity. Bioresource Technology 270, 216 – 222.